Condensed Multiwalled Carbon Nanotubes as Super Fibers

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Abstract

The ultra-low intershell shear strength in carbon nanotubes (CNTs) has been the primary obstacle to applications of CNTs as mechanical reinforcements. In this paper we propose a new CNT-system composed of comprising of coaxial cylindrical shells of sp^2-bonded carbons with condensed intershell spacings. Our atomistic calculations show that such condensed multiwalled carbon nanotubes (CMWNTs) can greatly enhance intershell shear strengths by several orders, and can simultaneously generate higher tensile strengths and moduli respectively than those of ordinary CNTs. It has further shown that CMWNTs can maintain thermally stable up to 2,000 K. By taking advantage of the primary enhancement mechanism of CMWNTs, a method of producing CMWNTs is therefore proposed tentatively. It is believed that CMWNTs featured with those properties can be taken as excellent candidates of super fibers for creating space elevators.

It may sound a crazy idea to build up a space elevator for delivering payloads from the Earth into space, the ultimately extra-low delivering cost, possibly US$10 per kilogram, makes space elevator as the only technology for exploiting solar power in a big way that could significantly brighten the world's dimming energy outlook [1]. To meet the biggest challenges of building a space elevator, the key issue lies in creating a superstrong, lightweight cable that can stretch over 36,000 km between the Earth and a geostationary space station. This requires at the minimum a specific tensile strength (namely the tensile strength-specific gravity ratio) of 48.5 GPa (for the graphite specific gravity 2.25), much higher than those of all natural or_artifical materials, e.g. 1.36 GPa for graphite whiskers, or 0.08 GPa for high carbon steel wires, before the discovery of carbon nanotubes (CNTs) [2]. It is known that sp^2 or carbon-carbon bond is the strongest bond in the nature. A single-walled carbon nanotube (SWNT) can be viewed as a cylindrical shell of sp^2-bonded monolayered carbon atoms, and a multi-walled carbon nanotube (MWNT) an assembly of SWNT-like shells with interwall spacings ~ 0.34 nm in average. Both experimental investigations [3, 4] and atomic simulations [5, 6, 7] using molecular dynamics or first-principals indicate that CNTs have a tensile Young's modulus of ~ 1 TPa (10^{11} Pa), and atomic simulations further show that ideal or defect-free CNTs can have a tensile failure strain as high as 16 to 24% [6, 8, 9]. These would give the pristine CNTs a specific tensile strength of 70 to 100 GPa, which can meet the requirement of space elevator. Wide discrepancy, however, exists between the theoretical and experimental results of CNT's failure strain and tensile strength. The most extensive fracture measurements of MWNTs [4] have shown that failure strains are ranged from 2 to 13% with the MWNTs breaking in the outermost wall. Quantum mechanical calculations [10] have explained the markedly reduced failure strain with vacancy defects and, in particular, large holes. And to understand the fractional breaking, Yu *et al.* [4] have found that the intershell shear strength is ultra-low and predominantly originated from the van der Waals interactions, with a value of 0.3 MPa comparable to the shear strengths (0.25 to 0.75 MPa) of high quality crystalline graphite. Similar ultra-low intershell shear strength (0.66 MPa) of MWNTs has also been estimated by Cumings and Zettl [11] in their discovery of reversible telescopic extensions. The intertube shear strength of CNT-ropes is of the same order or even lower than the intershell shear strengths of MWNTs. Although the above-mentioned findings have inspired many applications including ultra-low friction bearing [11] and gigahertz oscillators [12], the ultra-low intershell shear strength allows only

negligible load to be transferred from the outermost shell of MWNTs to the inner ones in spite of the fact that a typical MWNT contains dozens of walls. This understanding reveals a crucial mechanism that prevents the creation of CNT-reinforced composites with super strength.

Approaches have been progressively proposed for improving the intershell or intertube load-transfer properties of CNTs, which can be categorized according to two different mechanisms. The basic secrets of spun-yarn mechanism were discovered long ago and indicated by archaeological evidences from the late Stone Age. That mechanism was realized by Jiang *et al.* [13] in the creation of macroscopic self-assembled yarns, which were drawn out and spun directly from superaligned arrays of CNTs. The molecular mechanics simulations by Qian *et al.* [14] on a CNT rope comprising seven close-packed SWNTs predicted that a remarkable enhancement of the intertube load transfer property could be achieved by twisting the rope. The subsequently measured tensile specific strength (0.31 to 0.58 GPa) of the spun MWNT yarns by Zhang *et al.* [15], however, turn out not as much enhanced as expected from the mechansim put forward by Qian [14], and the Young's modulus of the spun yarns of CNTs may reduce to lower than one-tenth of that of straight CNTs [15, 16]. The second mechanism can be named as crosslink. Kis *et al.* [17] achieved a breakthrough by using moderate electron-beam irradiation inside a transmission electronic microscopy to generate crosslinks between the tubes, effectively eliminating sliding between the nanotubes and leading to a 30-fold increase of the bending modulus. In the light of abinitio total energy density functional theory, da Silva *et al.* [18] showed that Wigner defects existing in SWNT bundles could form a strong link between nanotubes and increase the shear modulus by a sizable amount. Huhtala *et al.* [19] suggested using small-dose electron or ion irradiation to partially transfer the load to the inner shell of double-walled carbon nanotubes, and their molecular-dynamics simulations showed that a small number of defects could increase the interlayer shear strength by several orders of magnitude. On the other hand, however, the coexisting vacancy defects and holes induced during irradiation may significantly (by 30% to 90%) reduce the tensile strength down to the same level as that of existing commercial carbon fibers [10, 20]. Furthermore, it was found that interstitial-vacancy pairs (or Wigner defects) as crosslinks were thermally instable - they will disappear at temperatures around just 500 K [21]. Nevertheless, all methods proposed by now can not enhance the interwall or intertube shear strengths by several orders of magnitude without remarkably reducing the

tensile strength and/or tensile stiffness.

Stimulated by the above-mentioned observations, we propose a new type of CNTs called condensed multiwalled carbon nanotubes (CMWNTs), which are composed of ideal or defect-free coaxial cylindrical shells of sp^2-bonded carbon atoms with interwall spacings smaller than those (about 0.34 nm) observed in ordinary MWNTs. Since sp^2-bond is physically valid for interwall spacings lowered down to 0.16˜0.18 nm [22]. our idea of CMWNTs is illuminated by the validity of thin-shell model of SWNTs [6, 24], in which the representative thickness about 0.066 nm was much smaller than the mean interwall spacing 0.34 nm, and which was also valid for modeling various complex mechanical behaviors.

Investigations on a six-walled zigzag CMWNTs - (5,0)@(11,0)@(17,0)@(23,0)@(29,0)@(34,0) were first conducted using the recently proposed second-generation reactive empirical bond order (REBO) potential [22], in which both the covalent bonding and van der Waals interactions into account. We modeled a supercell of the CMWNT containing 30 lattice loops in the axial directioin or having an axial length of about 4.26 nm. Our calculations showed that the energy-optimized configuration of the CMWNT, under the constraint that the six constituent shells are consistently elongated or shortened, has indeed compressed interwall spacings of 0.248, 0.256, 0.263, 0.272, 0.283 nm successively from the innermost shell (Shell 1) to the outermost one (Shell 6) as depicted in Fig. 1. To estimate the intershell shear strengths, we axially slided the ith shell relatively to the others and then calculated the energy fluctuation W_i versus the slide distance x. The force fluctuation F_i is valued as $-dW_i/dx$ and the force amplitude $F^i_{\max}$ should be balanced by the intershell shear strengths as follows: $F^i_{\max} = \tau_{i-1,i}A_{i-1,i} + \tau_{i,i+1}A_{i,i+1}$, where $\tau_{j,j+1}$ and $A_{j,j+1}$ denote the intershell shear strength and the middle surface area between the jth and $(j+1)$th shells with the conventions $\tau_{0,1} = \tau_{6,7} = 0$. The estimated values of the five intershell shear strengths are plotted in Fig. 1. For comparison, the intershell shear strength of the ordinary zigzag double-walled carbon nanotube (DWNT) - (10,0)@(19,0) - with the interwall spacing of 0.353 nm, is estimated to be 0.043 GPa, which is consistent with other theoretical predictions [23]. The results indicate that the intershell shear strength of the investigated CMWNT are in fact, enhanced greatly, by 40 to 380 times. Interestingly, the simulated intershell shear strengths $\tau(s)$ exponentially depend upon the interwall spacings s as follows $\tau(s)/\tau(s_0) = \exp(21.72\frac{s_0-s}{s_0})$, where $\tau(s_0) = 0.0453$ GPa and $s_0 = 0.34$ nm. This observation suggests a possibility of tremendous enhancement achieved by further

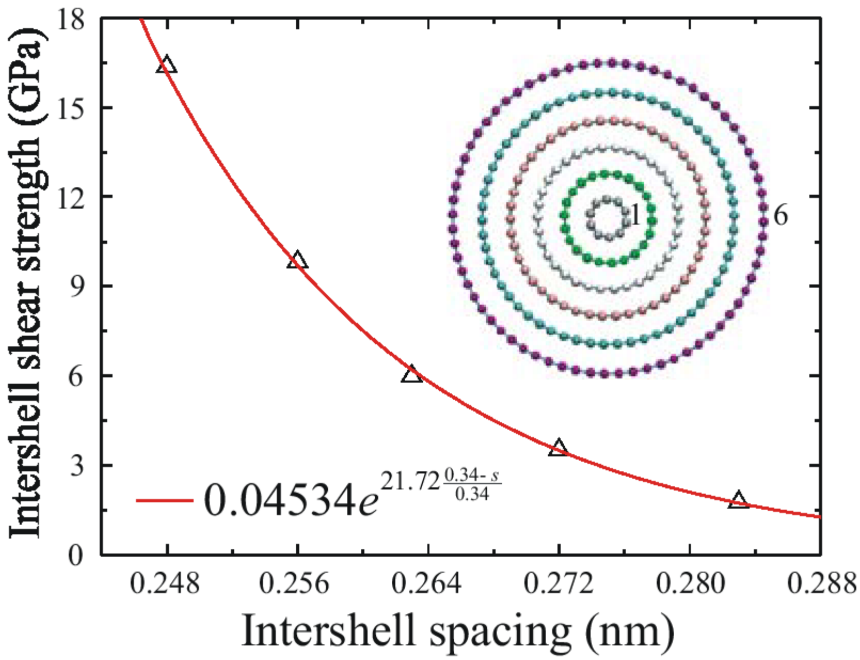

FIG. 1: Simulated intershell shear strength versus the compressed interwall spacing (triangles) following an exponential dependence (fitted line). Insert: the energy-optimized configuration of the CMWNTs

compressing the interwall spacing.

As mentioned previously, excellent tensile strength, superior tensile stiffness, and proper thermal stability are considered a must for the CMWNTs to become superfibers. To analyze those properties of the investigated CMWNT, we calculated the pulling force when elongating the surpercell and then evaluate the nominal stress σ defined as the pulling force divided by the representative cross-section area: $A = \frac{\pi}{4}(D_6 + \bar{s})^2$, where D_6 (= 3.0 nm) is the diameter of the outermost shell (34,0) and $\bar{s}$ (= 0.2644 nm) the average interwall spacing. The calculated σ versus the tensile strain or relative elongation ϵ for the investigated CMWNT is plotted in Fig. 2. For comparion, the $\sigma - \epsilon$ curves of the SWNTs (5,0), (11,0), ..., (34,0) with the assigned representative wall thickness 0.34 nm are also calculated and illustrated in Fig. 2, in good agreement with those reported by [10]. We note that the CMWNT has a failure strain ($\epsilon_{\rm cr} = 18\%$) almost the same as those of the SWNTs while its failure stress or tensile strength is even 20% higher than those of the SWNTs. This observation is exciting, in contrast to the existing methods or techniques for enhancing intershell shear strengths, which always suffer too much tensile strength loss. Furthermore, the Young's modulus Y

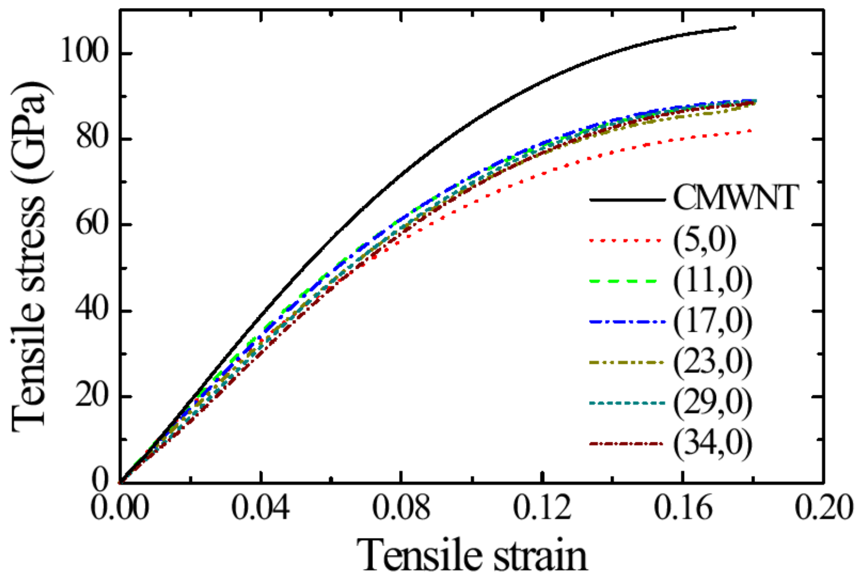

FIG. 2: $\sigma - \epsilon$ curves of the investigated CMWNT and its six constituent shells as individual SWNTs.

valued as the slope of the $\sigma - \epsilon$ curve at $\epsilon = 0$, namely $Y = \frac{d\sigma}{d\epsilon}|_{\epsilon=0}$, of the CMWNT is found larger than those of the SWNTs by 21.8%. Since the basal Young's modulus of graphite and the axial tensile modulus of SWNTs are approximately 1 TPa, the largest Young's modulus of all existing materials, our proposed CMWNT proves to be an uttermost material in respect of both tensile modulus and tensile strength.

To understand the mechanism of intershell-shear-strength enhancement, we modeled the constituent shells of the investigated CMWNT as isotropic elastic thin-shells [6, 24]. Comparing the diameters of the constituent shells in the optimized configuration of the investigated CMWNT with those of these shells in their respective SWNT states, we found that these shells sustain the circumferential self-equilibrum strains ε of -8.13%, -4.65%, 2.69%, 5.13%, 7.33%, and 9.64%, respectively, all below the failure strain limit (about 18%) range. Notably the innermost two shells are circumferentially compressed and others extended. As a rough estimate, the circumferential membranous force per unit axial length sustained by the ith shell is $N_i = Yt\varepsilon_i$, which is balanced by the radial pressure difference in the form $2N_i = p_{i-1,i}D_{i-1,i} - p_{i,i+1}D_{i,i+1}$, where $Yt = 0.34$ TPa $\times$ nm is the tensile rigidity, and $p_{j,j+1}$ and $D_{j,j+1}$ respectively the interwall pressure and middle surface diameter between the jth and $(j+1)$th shells as schematically illustrated in Fig. 3(a). With the radially

free-constraint condition $p_{6,7} = 0$ the interwall pressures $p_{j,j+1}$ for $j = 1, 2, ..., 5$ are thus estimated respectively as 173.3, 121.98, 73.08, 40.15, and 17.66 GPa, approximately exponentially dependent to the compressed interwall spacings. Our direct atomic calculations using the van der Waals forces between interwall carbon atoms result in interwall pressures of 113.6, 78.16, 52.50, 33.54, and 17.82 GPa respectively. The existence of these very high interwall pressures is very likely the primary mechanism of enhancing the intershell shear strength. Particularly, the following two phenomena which appeared in the above-mentioned observations interested us. First, the existence of pressure of the order of magnitude 100 GPa between two adjacent core shells implies that CMWNTs may not stably exist without a very small core. To ascertain this point, we study the two- to five-walled tubes generated from the investigated CMWNT by drawing out different numbers of the inner shells, and showed their energy-optimized configurations in Fig. 3(b) . The collapsed configurations for the two- to four-walled tubes only yield insignificantly enhancing effects on the interwall shell strength compared with those of ordinary MWNTs. Second, it is known that a pressure as high as several to dozens GPa may lead to a sp^2-sp^3 transition [25]. It is natural to question the thermal stability of CMWNTs as highly strained structures. To analyze this problem we performed atomistic simulations under canonical ensemble with various temperatures. As a result, the investigated CMWNT as a strained sp^2-bonded structure remains stable up to $2,000$ K within hundreds of picoseconds. Above this critical temperature the sp^2-bonded innermost shell (5,0) was transformed into sp^3-bonded or diamond nanowire; and above $3,000$ K the two-walled core (5,0)@(11,0) was transformed into diamond nanowire. It is found through further observations that the annealed diamond nanowires produced this way are stable. This study exhibits a new method for producing diamond nanowires without an extra-high external pressure.

The measurements of slide frictions between two relatively rotated contacting layers of graphite [26] show obvious dependence on the rotation angle, with a remarkable peak corresponding to zigzag commensuration. Similar observations were reported for the great commensurating dependence of intershell shear strength of DWNTs [23]. In order to compare the enhancement effects of commensuration, we investigated the zigzag double-walled tubes (10,0)@(16,0), (10,0)@(17,0), (10,0)@(18,0), and (10,0)@(19,0), as well as chiral commensurated ones (11,2)@(10,10), (11,2)@(11,11), and (11,2)@(12,12). Our calculated results of intershell shear strength versus intershell spacing are presented in Fig. 4, where the solid

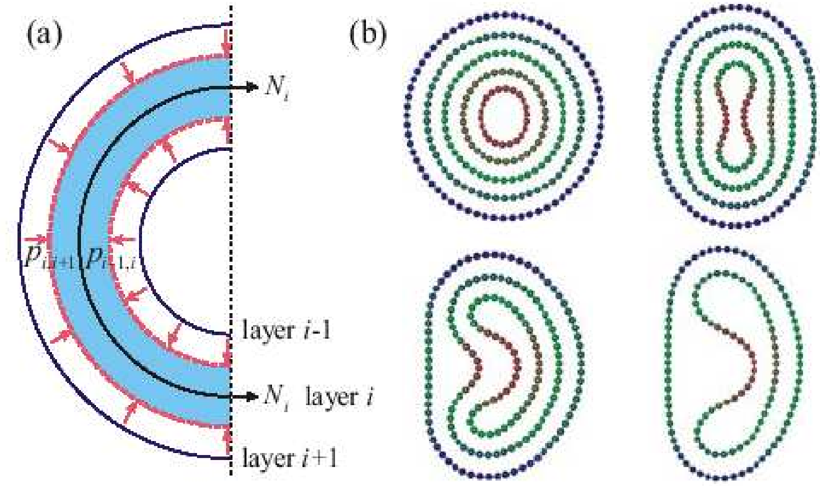

FIG. 3: Enhancement mechanism and instability. (a) Balance of circumferential force N_i and interwall pressures $p_{i-1,i}$ and $p_{i,i+1}$; (b) Energy-optimized Configurations of the five- to two-walled tubes generated by drawing out the inner one to four shells from the investigated CMWNT.

lines are fitted exponential dependence laws $\tau(s) = 0.0421\exp(53.79(0.353 - s))$ GPa for the zigzag tubes and $\tau(s) = 0.000469\exp(95.08(0.341 - s))$ GPa for the chiral ones respectively. The former is quite closed to the exponential law of the investigated six-walled zigzag CMWNT. This observation indicates that the exponential law is approximately independent of the number of walls. More interestingly, we find that the enhancing effect of spacing-compression on the chiral tubes is much larger than those of the zigzag ones. Although the intershell strength of the ordinary zigzag DWNT (10,0)@(19,0) differs from that of the chiral one (11,2)@(12,12) by two orders, it is expected that the intershell strengths of the condensed zigzag and chiral DWNTs with the diameter about 0.22 nm would become almost the same. In other words, the chirality effect on enhancement of intershell strength of CMWNTs appears to be insignificant.

Finally, we would conclude this report by proposing a method of producing CMWNTs, called irradiation-reconstruction process. Using electron irradiation within certain temperature circumstances ($\sim 600\ ^\circ$ C), Banhart *et al.* [27] found that ordinary carbon onions as assmeblies of concentric spherical shells of sp^2-bonded carbons with interwall spacings about 0.34 nm, could be transformed into condensed carbon onions with the observed interwall spacings of 0.22 to 0.28 nm. The compressing mechanism can be explained as the

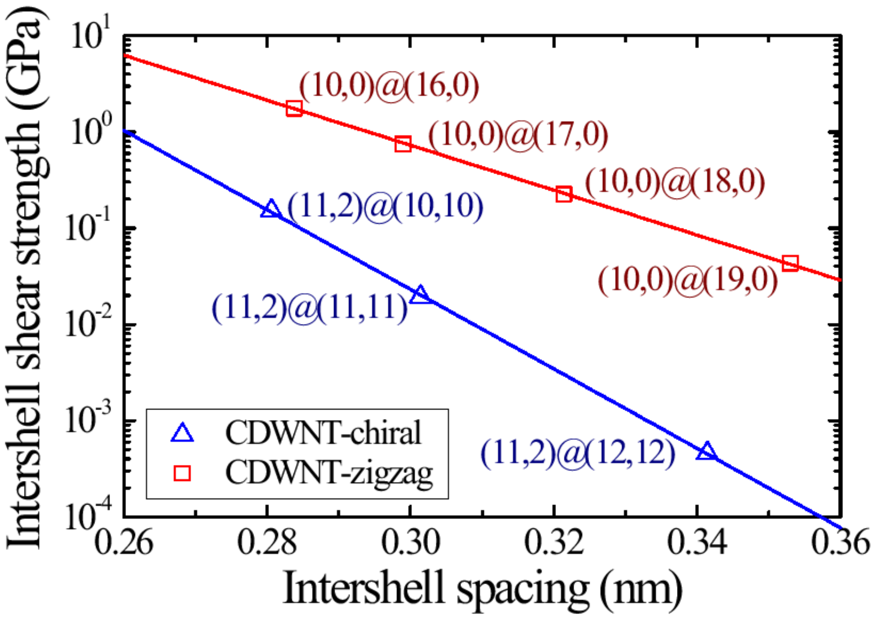

FIG. 4: Chirality effect on enhancement of intershell shear strnghth. The enhancement of intershell strength for the four zigzag CDWNTs and that for the three chiral ones follow different exponential laws.

following that electron-beam irradiation can knock off atoms of carbon onions in equilibrium state, thus inducing defects and vacancies. Since entirely sp^2-bonded is most energy-favored, anneal reconstruction could circumferentially shrink the constituent shells and generate very high intershell pressure because of the nanoscale shell diameters. Our further molecular dynamics calculations have confirmed that this mechanism is also valid for producing CMWNTs, indicating that CMWNTs could be low-costly produced. Therefore, CMWNTs could not only serve as the excellent candidates for manufacturing space elevators but also promise wide applications in producing super-reinforced composites.

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